

**TROPOSPHERIC CHEMISTRY STUDIES USING OBSERVATIONS  
FROM GOME AND TOMS**

NASA Grant NAG1-2153

Final Report  
For the period 1 January 1999 through 30 September 2002

Principal Investigator  
Kelly Chance

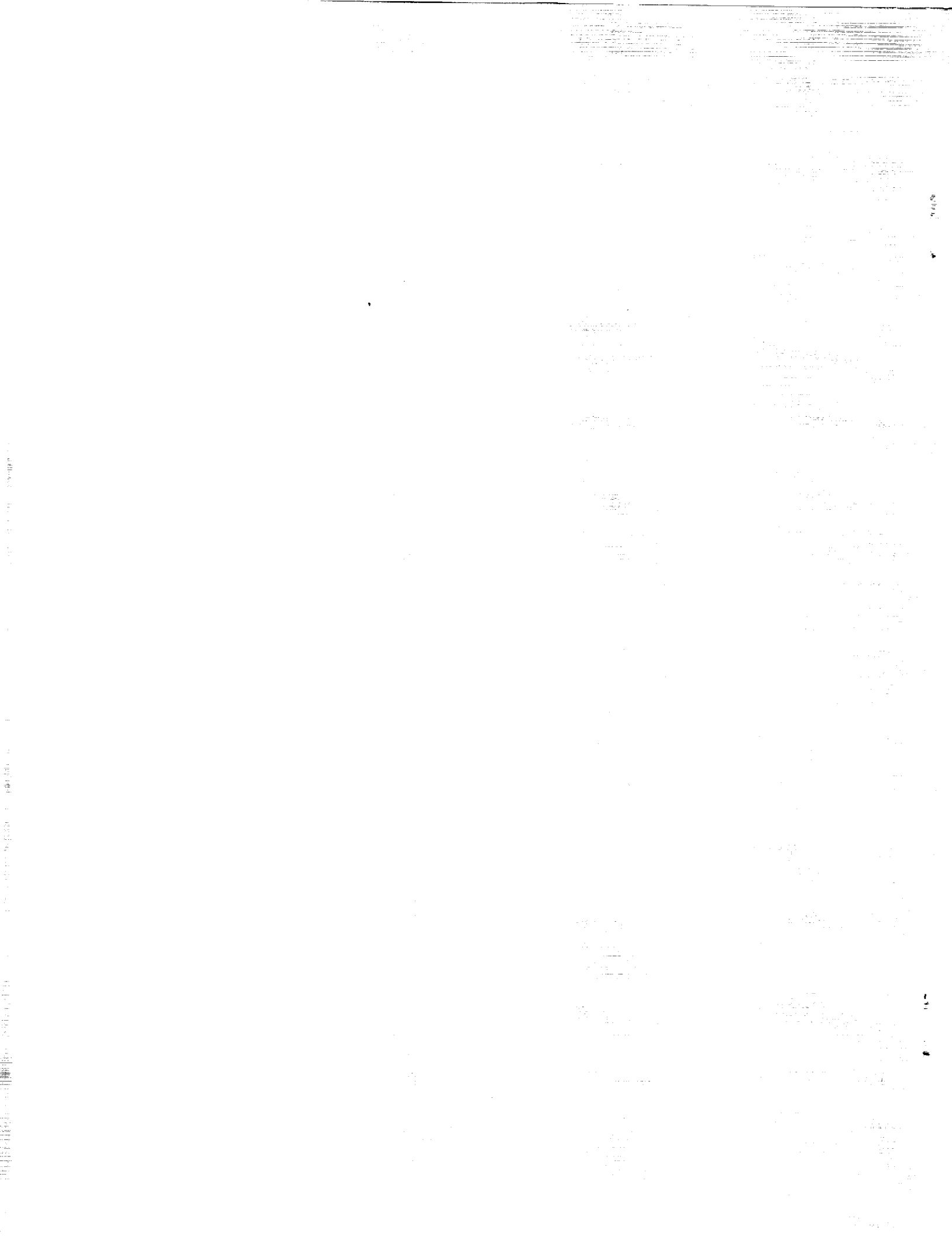
January 2003

Prepared for  
National Aeronautics and Space Administration  
Washington, DC 20546

SMITHSONIAN INSTITUTION  
ASTROPHYSICAL OBSERVATORY  
CAMBRIDGE, MASSACHUSETTS 02138

Director: Irwin I. Shapiro

The Smithsonian Astrophysical Observatory  
is a member of the  
Harvard-Smithsonian Center for Astrophysics



# **Tropospheric Chemistry Studies Using Observations From GOME and TOMS: An ACMAP Proposal**

## **Final Report NAG1-2153**

### **Principal Investigator**

Dr. Kelly Chance  
Smithsonian Astrophysical Observatory  
Atomic and Molecular Physics Division

### **Co-Investigators**

Dr. Robert J.D. Spurr  
Smithsonian Astrophysical Observatory  
Atomic and Molecular Physics Division

Dr. Thomas P. Kurosu  
Smithsonian Astrophysical Observatory  
Atomic and Molecular Physics Division

Prof. Daniel J. Jacob  
Department of Earth and Planetary Sciences and  
Division of Engineering and Applied Science  
Harvard University

Dr. James F. Gleason  
Laboratory for Atmospheres  
Atmospheric Chemistry and Dynamics Branch  
NASA Goddard Space Flight Center

## 1 Research Objectives

To quantitatively determine trace gas and aerosol amounts from the Global Ozone Monitoring Experiment (GOME) and the Total Ozone Monitoring Experiment (TOMS) and perform chemical modeling studies which utilize these results. This includes:

1. Analysis of measurements from the GOME and TOMS instruments for tropospheric distributions of  $\text{O}_3$  and  $\text{HCHO}$ ; tropospheric enhancements of  $\text{SO}_2$ ,  $\text{NO}_2$ , and aerosols associated with major sources; and springtime events of elevated  $\text{BrO}$  in the lower Arctic troposphere.
2. Application of a global 3-dimensional model of tropospheric chemistry to interpret the GOME observations in terms of the factors controlling the abundances of tropospheric ozone and  $\text{OH}$ .

The goals of the present research are:

1. To determine global climatologies of trace species associated with ozone chemistry in the stratosphere and troposphere.
2. To better understand the role of transport from the stratosphere, export from polluted continents, and large-scale photochemistry in determining the abundances of tropospheric ozone.
3. To analyze changes in tropospheric chemistry associated with perturbing events, including volcanic eruptions, large-scale fires, and polar springtime halogen enhancements.
4. To use  $\text{HCHO}$  as a photochemical tracer of  $\text{OH}$  chemistry and hydrocarbon reactivity in the troposphere.

## 2 Summary of Progress and Results

### 2.1 $\text{HCHO}$

We concentrated as a first priority on the capability to retrieve formaldehyde ( $\text{HCHO}$ ) from GOME measurements in a stable fashion and with high precision. We have developed the ability to determine air mass factors (relating satellite-geometry slant column measurements to vertical column amounts) for arbitrary altitude distributions of  $\text{HCHO}$ . Our method combines

the use of the SAO multiple scattering model LIDORT [Spurr *et al.*, 2001] with shape factors for the HCHO distribution calculated using the GEOS-CHEM 3-D model of tropospheric chemistry and transport, driven by assimilated meteorological data. We completed the initial study, to determine the HCHO over North America in July, 1996, including comparison of the measured HCHO with modeling results, and validation of the GEOS-CHEM shape factors against measurements from the Southern Oxidants Study and the North Atlantic Regional Experiment. Two publications resulted from this work [Chance *et al.*, 2000; Palmer *et al.*, 2001].

We then developed a methodology for deriving emissions of volatile organic compounds (VOC) using space-based column observations of HCHO, and applied it to data from the GOME satellite instrument over North America during July 1996. The HCHO column is related to local VOC emissions, with a spatial smearing that increases with the VOC lifetime. Isoprene is the dominant HCHO precursor over North America in summer, and its lifetime ( $\sim 1$  hour) is sufficiently short that the smearing can be neglected. We use GEOS-CHEM to derive the relationship between isoprene emissions and HCHO columns over North America, and use these relationships to convert the GOME HCHO columns to isoprene emissions. We also use the GEOS-CHEM model as an intermediary to validate the GOME HCHO column measurements by comparison with in situ observations. The GEOS-CHEM model including the GEIA emission inventory for isoprene provides a good simulation of both the GOME data ( $r^2=0.69$ ,  $n=756$ , bias=+11%) and in situ summertime HCHO measurements over North America ( $r^2=0.47$ ,  $n=10$ , bias=-3%). The GOME observations show high values over regions of known high isoprene emissions, and a day-to-day variability that is consistent with the temperature dependence of isoprene emission. Isoprene emissions inferred from the GOME data are 20% less than GEIA on average over North America and twice those from the US EPA BEIS2 inventory. The GOME isoprene inventory when implemented in the GEOS-CHEM model provides a better simulation of the HCHO in situ measurements than either GEIA or BEIS2 ( $r^2=0.71$ ,  $n=10$ , bias=-10%). This work has produced one publication to date [Palmer *et al.*, 2003].

A study of HCHO concentrations over North America for various seasons and years, over the lifetime of the GOME instrument, remains in progress. The study of the seasonal variation provides further testing and validation of the GEOS-CHEM model for predicting tropospheric chemistry and pollution. Detailed measurements, from individual orbits of GOME, indicate significant hot spots of production and possibly transport of HCHO and its progenitors. We will study the photochemistry and transport of individual episodes in order to understand the production and evolution of HCHO, and VOC emissions, in detail.

## 2.2 NO<sub>2</sub>

We have developed a retrieval of tropospheric nitrogen dioxide columns from GOME that improves in several ways over previous retrievals, especially in the accounting of Rayleigh and cloud scattering [Martin *et al.*, 2002b]. Slant columns, which are directly fitted without low-pass filtering or spectral smoothing, are corrected for an artificial offset likely induced by spectral structure on the diffuser plate of the GOME instrument. The stratospheric column is determined from NO<sub>2</sub> columns over the remote Pacific Ocean to minimize contamination from tropospheric NO<sub>2</sub>. The air mass factor (AMF) used to convert slant columns to vertical columns is calculated from the integral of the relative vertical NO<sub>2</sub> distribution from GEOS-CHEM, weighted by altitude-dependent scattering weights computed with LIDORT, using local surface albedos determined from GOME observations at NO<sub>2</sub> wavelengths. The AMF calculation accounts for cloud scattering using cloud fraction, cloud top pressure, and cloud optical thickness from a cloud retrieval algorithm (GOMECAT). Over continental regions with high surface emissions, clouds decrease the AMF by 20-30% relative to clear-sky. GOME is almost twice as sensitive to tropospheric NO<sub>2</sub> columns over ocean than over land. Comparison of the retrieved tropospheric NO<sub>2</sub> columns for July 1996 with GEOS-CHEM values tests both the retrieval and the NO<sub>x</sub> emissions inventories used in GEOS-CHEM. Retrieved NO<sub>2</sub> columns over the United States, where NO<sub>x</sub> emissions are particularly well known, are within 18% of GEOS-CHEM columns and strongly spatially correlated ( $r^2=0.78$ ,  $n=288$ ,  $p<0.005$ ). Retrieved columns show more NO<sub>2</sub> than GEOS-CHEM columns over the Transvaal region of South Africa, and industrial regions of the northeast United States and Europe. They are lower over Houston, India, eastern Asia, and the biomass burning region of central Africa, possibly because of biases from absorbing aerosols.

### **Inventory of Nitrogen Oxide Emissions Derived from Space-based Observations of NO<sub>2</sub> Columns.**

We then constructed a global inventory of NO<sub>x</sub> emissions using top-down information from our retrieval of tropospheric NO<sub>2</sub> columns from GOME. We combine the top-down information with an *a priori* bottom-up inventory weighted by relative errors in the top-down and bottom-up sources. The *a priori* inventory is based on the Global Emission Inventory Activity (GEIA) and scaled to 1996-97. Our GOME NO<sub>2</sub> retrieval was further improved by accounting for scattering and absorption of radiation by aerosols. Absorbing aerosols can decrease the sensitivity of GOME to tropospheric NO<sub>2</sub> over biomass burning regions by 40%. The air mass factor calculation in the retrieval uses local relative vertical profiles (shape factors) of NO<sub>2</sub> from GEOS-CHEM using the *a priori* inventory; application of a globally uniform shape factor would introduce regional biases of up to 40% over industrial regions and a factor of 2 over remote regions. We use the GEOS-CHEM model to calculate the local relationship between NO<sub>2</sub> columns and NO<sub>x</sub> emissions. Monthly mean top-down errors in NO<sub>x</sub> emissions of 50% at 2°×2.5° resolution are

comparable to bottom-up errors over industrial regions and much better elsewhere. Global a posteriori errors are about half of *a priori* errors. Global annual land surface NO<sub>x</sub> emissions for the *a priori*, a recent bottom-up inventory (EDGAR 3.0), and the a posteriori are 34.2, 36.2, and 35.1 Tg N yr<sup>-1</sup> respectively. Local a posteriori NO<sub>x</sub> emissions suggest underestimates of up to a factor of 2 near Johannesburg, Tehran, and Riyadh, up to 50% for Spain, Tokyo, and the Po Valley of Italy, and 25% for the eastern United States, as well as local overestimates of up to 50% for India and the biomass burning regions of central Africa and Brazil. The a posteriori inventory is more consistent with EDGAR than with the *a priori*. Anthropogenic a posteriori emissions are aseasonal despite seasonal variation in NO<sub>2</sub> columns. A posteriori NO<sub>x</sub> emissions provide evidence that soil NO<sub>x</sub> emissions are underestimated for the western United States, Spain, the Sahel, and the Mediterranean coastal region.

## 2.3 BrO

Studies of tropospheric BrO, including background concentration and springtime events of elevated BrO in the lower Arctic troposphere are ongoing, in collaboration with the Georgia Institute of Technology.

## 3 Journal Publications

Satellite Observations of Formaldehyde over North America from GOME, K. Chance, P.I. Palmer, R.J.D. Spurr, R.V. Martin, T.P. Kurosu, and D.J. Jacob, *Geophys. Res. Lett.* 27, 3461-3464, 2000.

A Linearized Discrete Ordinate Radiative Transfer Model for Atmospheric Remote Sensing Retrieval, R.J.D. Spurr, T.P. Kurosu, and K. Chance, *J. Quant. Spectrosc. Radiat. Transfer* 68, 689-735, 2001.

Air Mass Factor Formulation for Spectroscopic Measurements from Satellites: Application to Formaldehyde Retrievals from the Global Ozone Monitoring Experiment, P.I. Palmer, D.J. Jacob, K. Chance, R.V. Martin, R.J.D. Spurr, T.P. Kurosu, I. Bey, R. Yantosca, A. Fiore, and Q. Li, *J. Geophys. Res.* 106, 14,539-14,550, 2001.

Interpretation of TOMS Observations of Tropical Tropospheric Ozone with a Global Model and In-situ Observations, R.V. Martin, D.J. Jacob, J.A. Logan, I. Bey, R.M. Yantosca, A.C. Staudt, Q. Li, A.M. Fiore, B.N. Duncan, H. Liu, P. Ginoux, and V. Thouret, *J. Geophys. Res.* 107, 4351, doi:10.1029/2001JD001480, 2002a.

An Improved Retrieval of Tropospheric Nitrogen Dioxide from GOME, R.V. Martin, K. Chance, D.J. Jacob, T.P. Kurosu, R.J.D. Spurr, E. Bucsela, J.F. Gleason, P.I. Palmer, I. Bey, A.M. Fiore, Q. Li, and R.M. Yantosca, *J. Geophys. Res.* *107*, 4437, doi:10.1029/2001JD001027, 2002b.

Tropospheric Chemistry Measurements from the GOME and SCIAMACHY Instruments, K. Chance, T. Kurosu, R. Spurr, C. Sioris, R. Martin, P. Palmer, A. Fiore, and D. Jacob, *Proc. S.P.I.E., Remote Sensing of Clouds and the Atmosphere VII*, 4882, paper 43, 2002.

Mapping Isoprene Emissions over North America using Formaldehyde Column Observations from Space, Palmer, P. I., D. J. Jacob, A. M. Fiore, R. V. Martin, K. Chance, and T. Kurosu, *J. Geophys. Res.*, in press, 2003.





